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The Radiolysis of Liquid Nitrogen Containing Hydrocarbons. II. Acetonitrile Formation from the Solution of Ethylene

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The ^{60}Co γ-radiolysis of liquid nitrogen containing ethylene has been reinvestigated in order to elucidate the mechanism of the formation of nitrogenous products. When the conversion of ethylene was 10%, the *G*-values of hydrogen cyanide and acetonitrile were 0.21 ± 0.03 and 0.05 ± 0.01 respectively. The isotopic distributions in acetonitrile, *n*-butane, and acetylene were examined by using an equimolar mixture of C_2H_4 and C_2D_4 as the solute. From the analysis of these distributions, it has been concluded that acetonitrile is produced mainly from the reaction between nitrogen atoms and ethyl radicals.

Recently we have reported on our study of the radiolysis of liquid nitrogen containing small amounts of ethylene and propylene.[1] In the case of propylene, the only nitrogenous product observed was acetonitrile, most of which could be explained as resulting from the reaction between nitrogen atoms and propylene molecules. In the system of ethylene, however, the mechanism of the formation of the nitrogenous products, hydrogen cyanide and acetonitrile, could not be ascertained in the previous experiment. We have, therefore, reinvestigated the liquid nitrogen-ethylene system more thoroughly and have now been able to elucidate the mechanism of the formation of acetonitrile in some detail.

Experimental

Nitrogen gas of a high purity was purchased from the Nippon Sanso Co. Fully-deuterated ethylene C_2D_4 was synthesized from C_2D_2,[2] which had been synthesized from CaC_2 and D_2O. The nitric oxide, carbonyl sulfide, and ordinary ethylene were purchased from the Takachiho Chemical Industrial Co.

The samples were prepared and irradiated in the same manner as has been previously described.[1] For the determination of isotopic species, a mass-spectrometric analysis was made at a voltage near the appearance potential of the respective parent ions after separating the products with a gas chromatograph (a dioctyl phthalate column for acetonitrile and benzyl ether for acetylene and butane).

The rest of the procedure was similar to that previously described.[1]

Results

To assure the homogeneity of the reaction, the yields of hydrogen cyanide and acetonitrile were measured with various amounts of liquid nitrogen. The results are shown in Fig. 1. Obviously the yields are directly proportional to the amount of liquid nitrogen. This supports the assumption that the reactions take place in the bulk. In order to examine the effect of any impurity in liquid nitrogen, several experiments were carried out by using liquid nitrogen preirradiated in the presence of ethylene, but such treatment did not affect the *G*-values of the nitrogenous products.

Figure 2 shows the *G*-values of the main products

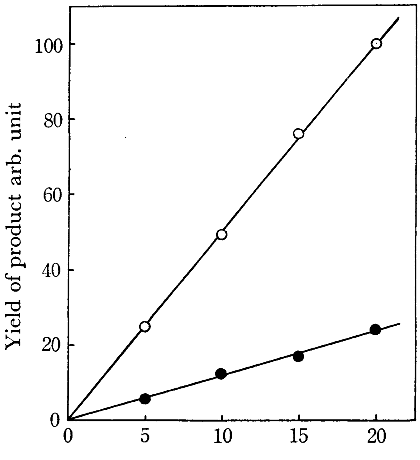

Fig. 1. Relative yields of hydrogen cyanide (○) and acetonitrile (●) as a function of the volume of liquid nitrogen. Ethylene concentration is 4×10^{-4} in mole fraction. Irradiation time is one hour.

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[1] T. Oka, Y. Suda and S. Sato, This Bulletin, **42**, 3083 (1969).

[2] Y. Hatano, S. Shida and S. Sato, *ibid.*, **41**, 1120 (1968).

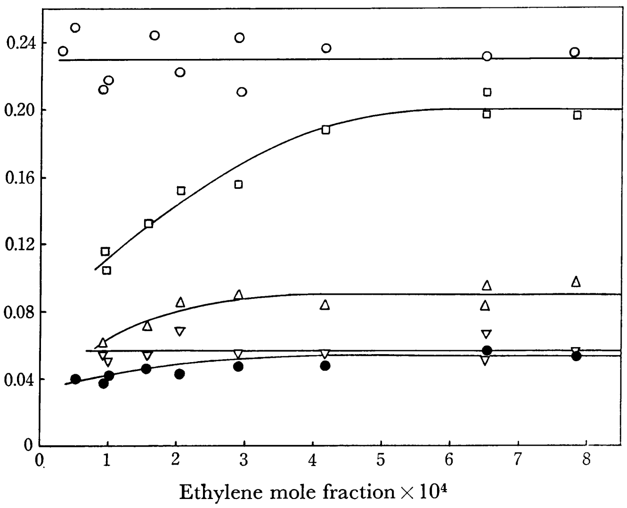

Fig. 2. G-values of hydrogen cyanide (○), ethane (□), acetylene × 1/10 (△), propane (▽) and acetonitrile (●) as a function of the concentration of ethylene. Volume of liquid nitrogen is 10 m*l* and irradiation time is one hour.

as a function of the concentration of ethylene. The products other than those shown in Fig. 2 were *n*-butene, 1-butane, and hexenes. A small amount of a paste-like material which may consist of more than two compounds was also formed. A part of it at least was yellow-colored and was soluble in methanol.

The G-values of ethane and acetylene decreased with a decrease in the concentration of ethylene. The G-value of acetonitrile also decreased slightly at the lower concentration. On the other hand, the G-values of hydrogen cyanide and propane were independent of the reactant concentration. The G-value of hydrogen cyanide was 0.21±0.03.

In order to check whether the decrease in the G-values of ethane and acetylene at lower concentrations of ethylene is due to the high conversion or to the consumption of the primary products by the secondary reactions, the irradiation time dependence of the yields of the products was measured at two concentrations, 1×10^{-4} and 6.5×10^{-4} in mole fraction. The results are shown in Figs. 3, 4, and 5. At lower concentrations, the yields of acetylene, ethane, and propane deviated from a linear relationship at one hour and the reactant

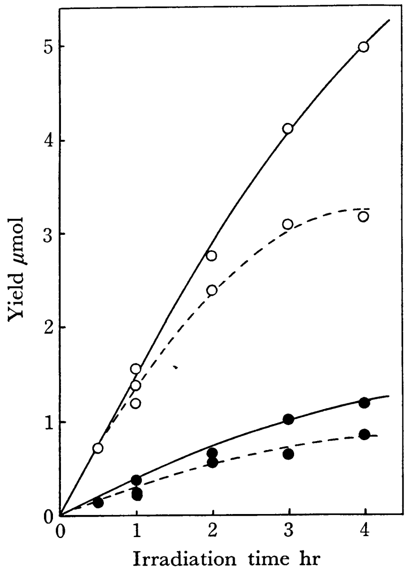

Fig. 3. Irradiation time dependence of the yields of hydrogen cyanide (○) and acetonitrile (●).
——, ethylene concentration is 6.5×10^{-4} in mole fraction.
------, 1.0×10^{-4} in mole fraction.

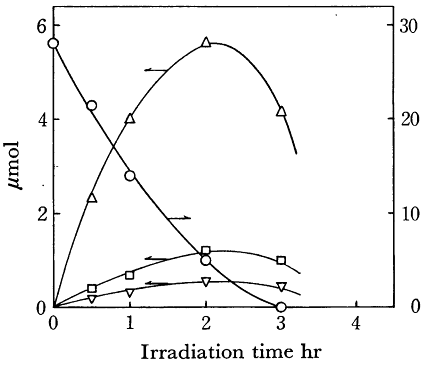

Fig. 4. Irradiation time dependence of the yields of acetylene (△), ethane (□) and propane (▽), and the amount of ethylene recovered (○). Initial ethylene concentration is 1.0×10^{-4} in mole fraction.

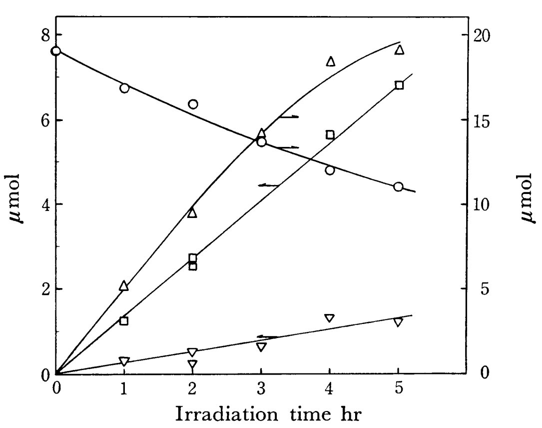

Fig. 5. Irradiation time dependence of the yields of acetylene (△), ethane (□) and propane (▽), and the amount of recovered ethylene × 1/10 (○). Initial ethylene concentration is 6.5×10^{-4} in mole fraction.

ethylene was almost completely consumed in three hours. At higher concentrations, the yields of all the products increased linearly up to about three hours and the conversion of ethylene in one hour was 10%. From these results, it may be concluded that the decrease in the G-values of ethane and acetylene at the lower concentrations of ethylene in Fig. 2 is not due to the high conversion.

Table 1. Hydrogen cyanide and acetonitrile from the radiolysis of liquid nitrogen containing equimolar mixture of C_2H_4 and C_2D_4

Run	G		Acetonitrile			
	Hydrogen cyanide	Acetonitrile	d_0	d_1	d_2	d_3
1 mix.	0.18_4	0.04_3	100	36	54	78
2 mix.	0.14	0.03_5	100	35	55	83
3 mix.	0.15_3	0.03_5	100	37	59	80
		mean	100	36±1	56±3	80±3
4 C_2D_4	0.09_3	0.04_9	1.9	2.9	2.9	100

Table 2. n-Butane and acetylene from the radiolysis of liquid nitrogen containing equimolar mixture of C_2H_4 and C_2D_4

n-Butane		Acetylene	
d_0	44±3	d_0	100
d_1	49±1	d_1	0
d_2	21±3	d_2	90±1
d_3	(0)		
d_4	74±2		
d_5	100		
d_6	37		
d_7	(0)		
d_8	32±2		
d_9	56±5		
d_{10}	23±4		

Tables 1 and 2 show the isotopic distributions of acetonitrile, n-butane, and acetylene obtained when an equimolar mixture of C_2H_4 and C_2D_4, and pure C_2D_4 were used as the solutes. The isotopic distribution of hydrogen cyanide could not be obtained, because the H–D exchange reaction took place during the gas-chromatographic analysis. For example, the hydrogen cyanide obtained in Run No. 4 in Table 1 should be DCN, but the mass-spectrometric analysis showed HCN only.

For acetonitrile such an exchange occurred to only a negligible extent, as is shown in Table 1. In spite of the possibility of experimental error, it may be said that the G-value of DCN from the C_2D_4 solution is lower than that of HCN from the C_2H_4 solution. The isotopic distributions of n-butane and acetylene shown in Table 2 are averages of three measurements. These values will be discussed in detail later.

Table 3. The effects of additives

Additive*	G					
	HCN	CH_3CN	C_2H_6	C_3H_8	n-C_4H_{10}	C_2H_2
none	0.19_4	0.04_2	0.18_7	0.06_8	0.06_8	0.79_8
8% NO	0.16	0.01_8	0.15_4	0.01	0.00_5	0.70
18% NO	0.10	0.01_5	0	0	0	0.65_6
14% COS	0.21	0.05_1	0.15_2	0.06_3	0.05_8	0.76_2
17% COS	0.21	0.04_7	0.17_3	0.03_8	0.03	0.77_7

* Per cent for ethylene of 6.5×10^{-4} m.f.

In Table 3, the effects of additives are summarized. Nitric oxide reduced the yields of all hydrocarbons except for acetylene to a large extent, and those of nitrogenous products to a certain extent. Carbonyl sulfide, which is now known as an electron scavenger in the condensed-phase radiolysis,[3] slightly reduced the yields of propane and n-butane.

Discussion

In a previous paper,[1] we have tentatively discussed the mechanism of the formation of nitrogenous products in the radiolysis of liquid nitrogen containing ethylene. We there suggested that the reaction between nitrogen atoms and ethyl radicals might be the only source of acetonitrile. Since the n-butane obtained in the present system is believed to be formed by the combination reaction of two ethyl radicals,[1] the isotopic distributions of n-butane and acetonitrile from solutions containing equimolar mixtures of C_2H_4 and C_2D_4 should have a certain relationship if the acetonitrile is

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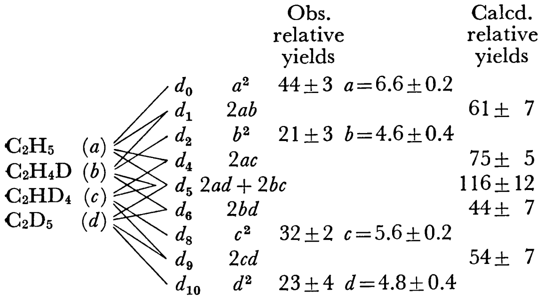
[3] S. Hirokami, S. Shishido and S. Sato, *ibid.*, **43,** 973 (1970).



				Obs. relative yields		Calcd. relative yields
		d_0	a^2	44±3	$a=6.6\pm0.2$	
		d_1	$2ab$			61± 7
C_2H_5	(a)	d_2	b^2	21±3	$b=4.6\pm0.4$	
C_2H_4D	(b)	d_4	$2ac$			75± 5
C_2HD_4	(c)	d_5	$2ad+2bc$			116±12
C_2D_5	(d)	d_6	$2bd$			44± 7
		d_8	c^2	32±2	$c=5.6\pm0.2$	
		d_9	$2cd$			54± 7
		d_{10}	d^2	23±4	$d=4.8\pm0.4$	

Scheme 1

produced by the reaction between nitrogen atoms and ethyl radicals.

The ethyl radicals formed by γ-irradiation in liquid nitrogen containing a mixture of C_2H_4 and C_2D_4 may be expected to be of four kinds, shown in the first column in the scheme 1 of calculation. Here, the *a*, *b*, *c*, and *d* in parentheses denote the relative concentrations. The relative amounts of isotopic *n*-butanes formed on the combination of ethyl radicals are those in the fourth column. Butane-d_3 and -d_7 are probably not formed; this is in agreement with the experimental data. Now, let us introduce from Table 2 the experimental values for a^2, b^2, c^2, and d^2; then we can calculate the relative yields of the isotopic ethyl radicals, *a*, *b*, *c*, and *d*. The results are shown in the sixth column. By using these values, we can calculate the relative yields of butane-d_1, -d_4, -d_5, -d_6, and -d_9. The calculated values can then be compared with those shown in Table 2. The agreement is satisfactory.

If acetonitrile is formed by the following reaction; Ethyl radical + N→Acetonitrile + 2 Hydrogen atoms (1) the isotopic distribution of acetonitrile can be calculated by using the values for *a*, *b*, *c*, and *d*. However, in this calculation we need another assumption regarding the detachment of two hydrogen atoms in the reaction (1). We have calculated for two types of detachment:

1) Every hydrogen atom in an ethyl radical has an equal probability of detachment. On the basis of this assumption, the relative yields obtained for the isotopic distribution of acetonitrile are as follows:

d_0	d_1	d_2	d_3
100	33±5	40±4	83±11

These values are in good agreement with those shown in Table 1.

2) Two hydrogen atoms at the α position in ethyl radical preferentially detach in the reaction (1). In this case, the calculated results are as follows, far from the experimental data:

d_0	d_1	d_2	d_3
100	70±6	83±3	73±6

However, if a part of the acetonitrile is produced by such reactions as;

$$\text{Ethylene} + \text{N} \longrightarrow \text{Acetonitrile} + \text{Hydrogen atom} \qquad (2)$$

and;

$$\text{Vinyl radical} + \text{N} \longrightarrow \text{Acetonitrile} \qquad (3)$$

the relative yields of acetonitrile-d_0 and -d_3 will be increased and the isotopic distribution calculated will become consistent with the experimental data. The best-fit distribution was obtained by assuming that 65% of the acetonitrile is produced by the reaction (1) and the rest by the reaction (2) or (3) with the ratio of the isotope effect in the reaction (2) or (3) being 1 : 0.87 for d_0 : d_3. The obtained distribution is as follows:

d_0	d_1	d_2	d_3
100	36±3	44±2	80±3

Obviously, even when two α-positioned hydrogen atoms are detached in the reaction (1), it can be concluded the formation of acetonitrile is mainly due to the reaction (1), *i. e.*, the reaction of ethyl radicals and nitrogen atoms.

As is shown in Table 3, nitric oxide efficiently reduces the yields of ethane, propane, and *n*-butane. Since these hydrocarbon products are believed to be formed by the radical reactions, the above result indicated that nitric oxide is a radical scavenger, even at the temperature of liquid nitrogen. In the gas phase, nitric oxide is known as an effective scavenger for nitrogen atoms;[4)]

$$\text{N} + \text{NO} \longrightarrow \text{N}_2 + \text{O} \qquad (4)$$

The decrease in hydrogen cyanide and acetonitrile by the presence of nitric oxide is probably due to this reaction. However, if acetonitrile is formed solely by the reaction between nitrogen atoms and ethyl radicals, the presence of nitric oxide should reduce the yields of acetonitrile as much as that of *n*-butane, but acetonitrile was observed to the extent of $G=0.015$ even at the nitric oxide concentration, whereas the formation of *n*-butane was almost completely suppressed. This suggests that a part of the acetonitrile is produced by a process other than the reaction (1). In the preceding section, we have discussed two types of ethyl radical reactions producing acetonitrile; in the first, the hydrogen atom-detachment was indiscriminative, while in the second α-positioned hydrogen atoms were predominant in the detachment. Moreover, in the latter case a part of the acetonitrile formation has to be attributed to a process other than the reaction (1). If this is the reaction (2), the effect of nitric oxide on the formation of acetonitrile can be ex-

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[4)] P. Harteck, R. R. Reeves and G. Mannella, *J. Chem. Phys.*, **29**, 608 (1958).

plained consistently.*[1] A similar explanation may serve to explain the effect of nitric oxide on the formation of hydrogen cyanide; this product is formed by two processes, the one containing ethylene as the reactant, and the other containing methyl radicals, which are subject to the radical scavenging of nitric oxide:

$$C_2H_4 + N \longrightarrow HCN + CH_3 \qquad (5)$$

$$CH_3 + N \longrightarrow HCN + 2H \qquad (6)$$

Although the effect was small, the addition of COS reduced the yields of hydrocarbon products. Since COS is known to be an electron scavenger, even at the temperature of liquid nitrogen,[6] the participation of ionic species in the formation of propane and *n*-butane cannot be completely ruled out. However, the contribution of this type of reaction is obviously minor.

In the study of the argon-sensitized radiolysis of ethylene, Klassen found that $G(C_2H_2) \simeq G(C_2H_6) + G(n\text{-}C_4H_{10})$ and that $G(C_3H_8)$ is much smaller than $G(n\text{-}C_4H_{10})$.[7] The present system is similar to that of Klassen, the only difference being in the solvent, but the relative yields of the hydrocarbon products are quite different. For example, $G(C_2H_6)$ is much larger than $G(n\text{-}C_4H_{10})$ and $G(C_3H_8)$ is nearly equal to $G(n\text{-}C_4H_{10})$. These discrepancies may be explained by the reactions of radicals produced by the reactions (1), (2) and (5); that is, the following reactions become important in the present system:

$$H + C_2H_5 \longrightarrow C_2H_6$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8$$

$G(C_2H_2)$ is not affected by the presence of nitric oxide. The formation, therefore, can be explained by this reaction;

$$N_2{}^* + C_2H_4 \longrightarrow N_2 + C_2H_2 + H_2(\text{or } 2H),$$

which has already been discussed.[1]

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*[1] In the presence of nitric oxide, another source of acetonitrile is possible:[5] $C_2H_5 + NO \rightarrow C_2H_5NO \rightarrow CH_3CN + H_2O$. However, if this reaction should occur, the *G*-value of acetonitrile should be much larger than that observed.

5) G. L. Pratt and J. H. Purnell, *Trans. Faraday Soc.*, **60**, 371 (1964).

6) S. Mizutani and S. Sato, to be published.

7) N. V. Klassen, *J. Phys. Chem.*, **71**, 2409 (1967).